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Calix[4]resorcinolarenes with alkylphosphonic fragments: Protolytic properties and interaction with lanthanum(III)

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Abstract

The protolytic and complexing properties of phosphorylated derivatives of calix[4]resorcinolarenes were studied by pH-metric titration at 298 K in water-2-propanol (80 vol % 2-propanol). It was shown that calix[4] resorcinolarene containing the propylphosphonic acid fragment at the C atom linking the aryl groups exists in solution mainly as tetramer. At pH > 4, the anions of tetrameric, dimeric, and monomeric forms of this compound are formed. The neutral form of aminomethylated calix[4]resorcinolarene contaning, along with the propylphosphonic acid fragment, the CH2NEt2 group on the opposite side of the molecule is monomeric. It exists as a zwitterion and contains four betaine protons. Three dimeric species of this compound, one protonated and two deprotonated, were revealed. The dissociation constants of the phosphonate groups and two betaine protons were evaluated. The other two betaine protons and the protons of hydroxy groups do not dissociate. The equilibrium constants of the complex formation with lanthanum(III) and in some cases the stability constants of the complexes were calculated. Probable modes of coordination of calix[4]resorcinolarenes are discussed. Depending on the acidity of the medium, the competition between the phosphonic group and the phenolate ions takes place, and complexes with the coordination via phosphonic groups can rearrange into complexes with the coordination via phenolate groups. © Pleiades Publishing, Inc., 2006.

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